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Temperature dependence of the refractive index of diamond up to 925 K

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We have measured the refractive index n of diamond for temperatures up to 925 K from Fabry-Perot resonances in far-infrared transmission spectra. For the highest temperatures the data approach the regime where n varies almost linearly with T. In contrast to other investigations, this makes a precise extrapolation to $T=0$ K possible and allows us to determine the refractive-index renormalization Δn due to electron-phonon interaction and thermal expansion as well as an estimate of isotope effects on n. These data and values obtained for the thermo-optic coefficient $[(1/n)(\partial n/\partial T)]$ are compared to those of previous measurements and results from different theoretical approaches, such as empirical pseudopotential and *ab initio* calculations.

I. INTRODUCTION

Diamond is a prototype semiconductor whose fundamental properties and potential applications have been intensively investigated for a long time.[1] Among the recent highlights in *basic research* are the discovery of large phonon renormalization effects due to isotope disorder that have been observed in Raman[2,3] and cathodoluminescence spectra.[4] The band gap of diamond shifts considerably with the isotope mass.[5,4] The ground state of boron acceptors in diamond exhibits a fine structure[6,7] that is partly due to the reduced spin-orbit coupling in the acceptor compared to that of the bulk valence bands.[8] As far as *applications* are concerned, the enhanced thermal conductivity of isotopically pure diamond[9] with respect to the natural one has been exploited in mirrors for synchrotron radiation in order to avoid lattice distortions due to the large heat load.[10] The low absorption coefficient of diamond in the infrared region is beneficial for high-power applications like plasma heating where windows of synthetic polycrystalline diamond with diameters of several centimeters are nowadays being used.[11] Furthermore, diamond is being applied in high-temperature electronics.

In view of the existing wealth of information on diamond, it is quite surprising that not too much is known about one of its most important properties, namely the temperature dependence of the refractive index. While a single value of $(1/n)(\partial n/\partial T)=5\times10^{-6}$ at 300 K for the thermo-optic coefficient in the low-frequency limit has been published more than 40 years ago[12] and a few temperature-dependent values of n at visible wavelengths have been given even earlier,[13] the $n(T)$ data of Ref. 14, taken over the limited temperature range 5.5–340 K, have been the ‘‘standard’’ since 1977. Only very recently further contributions have appeared. These are a study of far-infrared Fabry-Perot transmission oscillations of a thin polycrystalline diamond plate with parallel surfaces [$295\ \mathrm{K}\leqslant T\leqslant 784\ \mathrm{K}$ (Ref. 15)], using the experimental approach employed here,[16] and a Brillouin scattering study [$300\ \mathrm{K}\leqslant T\leqslant 1600\ \mathrm{K}$] (Ref. 17)], which, however, only yields rather indirect information on $n(T)$ in the visible range.

The theoretical description of the refractive index and the thermo-optic coefficient in semiconductors presents a considerable challenge because it requires a reliable model for the dielectric function and its renormalization by the electron-phonon interaction and the thermal expansion of the lattice. For a wide range of materials, $(1/n)(\partial n/\partial T)$ has been calculated with empirical pseudopotentials in Ref. 18, and good agreement with experiments at 300 K was obtained. Recently, this problem has been addressed with *ab initio* methods for the elemental semiconductors C, Si, and Ge; the results also agree well with the experimental thermo-optic coefficients at 300 K.[19] However, due to the large Debye temperatures Θ_D of C [1880 K (Ref. 18) at room temperature (RT)], Si [647 K (Ref. 18) at RT], and, to a lesser extent, Ge [354 K (Ref. 18) at RT], room-temperature values of the thermo-optic coefficient are insufficient for reliable predictions of the refractive index at higher temperatures. The reason for this deficiency is that a linear approximation of $n(T)$ is only possible at temperatures much larger than Θ_D where the vibrational degrees of freedom can be described by a single ‘‘effective’’ phonon oscillator.

In view of the technological relevance of diamond in high-temperature applications, a precise measurement of its refractive index in this regime is very important. With regard to fundamental research, the knowledge of the thermo-optic coefficient in the linear (high-temperature) regime allows one to make an extrapolation and determine the refractive-index renormalization by the zero-point vibrations at 0 K. This quantity constitutes a critical test for theoretical predictions.[18,19] Furthermore, it also allows one to estimate the change of the refractive index with the carbon isotope mass, an analogous effect that results from the influence of the electron-phonon interaction and the thermal expansion on the electronic structure. A large isotope shift of $\Delta\epsilon/\epsilon=0.09\%$ (Ref. 20) for the relative change in the long-wavelength dielectric constant $\epsilon=5.7$ between ^{12}C and ^{13}C diamond has been predicted in Ref. 19. This should lead to a refractive-index difference of $\Delta n=0.0011$, an effect large enough to be measured by an interference technique.

To clarify these issues, we have measured the refractive

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index of natural diamond up to 925 K using far-infrared transmission Fabry-Perot oscillations. Details on the experiments and the data analysis are given in Sec. II. The results are discussed in Sec. III. Conclusions are given in Sec. IV.

II. EXPERIMENT

The sample investigated was a natural type-IIa diamond plate with $\langle 100 \rangle$ oriented faces, lateral dimensions of 10×10 mm^2, and a thickness of $d = 979.5(5)$ μm. The large flat surfaces, through which the measurements of Fabry-Perot interference fringes were performed, were parallel within 0.017° and polished to a precision of 3 nm average surface roughness. The far-infrared transmission was measured with the sample in thermal contact with the cold finger or heater of an evacuated cryostat using a Bruker IFS 113 V Fourier-transform spectrometer. Depending on the spectral range, a Si bolometer (30–700 cm^{-1}) or a Hg$_x$Cd$_{1-x}$Te detector (500–4000 cm^{-1}) was used for signal recording. The spectral resolution was set to 0.1 cm^{-1} in order to obtain the precise shape of the individual interference fringes. In view of possible measurements of small isotope shifts, we chose a spectral range where the refractive index is essentially free of dispersion. This is the case for frequencies below 1000 cm^{-1}, where n varies by less than 0.005%.[15]

Intuitively, the most precise determination of n should result from analyzing the largest number of Fabry-Perot fringes possible. From the fringe oscillation period P, obtained by Fourier transformation of the transmission data, the refractive index can be determined via $n = 1/(2dP)$. Unfortunately, however, the amplitude of the interference fringes is not constant over the spectral range of several hundred wave numbers measured. Instead, the data exhibit a slight decrease in oscillation amplitude towards higher frequencies due to approaching the two-phonon absorption bands as well as large-period beatings and other modulations. This reduces the precision in determining the oscillation period and thus the refractive index.

We have therefore chosen much smaller frequency intervals of about 25 cm^{-1} with almost constant Fabry-Perot oscillation magnitudes and fitted the data to the well-known Airy function, which for normal incidence transmission of a parallel plate reads

$$T(\nu) = \frac{1}{1 + F \sin^2(2\pi\nu n d)} + B, \tag{2.1}$$

where ν is the frequency in wave numbers. The free parameters finesse F, refractive index n, and offset B were determined by a nonlinear least-squares fit. The multiplicity of the argument in the sine of the Airy function was removed ''manually'' by considering only that value of n for which the variance between fit and data has the smallest value. Typical transmission curves (open circles) and fits (solid lines) for several temperatures are shown in Fig. 1. While the period of the oscillations hardly changes with temperature, the positions of the transmission extrema show systematic shifts, reflecting the increase of the optical path length in the sample with increasing T. All data presented here were obtained for the frequency range of 94-118 cm^{-1}, covering about eleven periods of the interference patterns. We also performed the data analysis in other frequency regions up to 600 cm^{-1} and verified that the results are unaffected by dispersion. However, systematic offsets between different temperature-dependent series of measurements occured, presumably due to slight changes in the sample positioning. These deviations did not exceed $\Delta n = 0.0025$ and were accounted for by normalizing all data to the room-temperature refractive index of $n_{300} = 2.387\,47$ from Ref. 14.

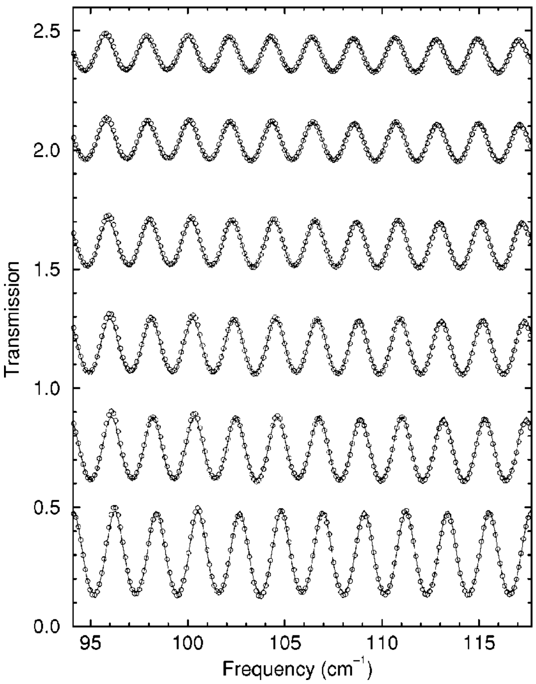

FIG. 1. Temperature-dependent transmission spectra (open circles) of diamond in the far-infrared region (from bottom to top: $T = 50$, 300, 400, 500, 600, 650 °C). The curves were vertically offset for clarity. The solid lines are Airy function fits to the data from which the refractive index has been determined (see Fig. 2).

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of the diamond refractive index with temperature. The thick solid line represents a fit of

$$n(T) = n_0 + A\left[n_{BE}(\hbar\omega, T) + \tfrac{1}{2}\right] \tag{3.1}$$

to the data (open circles) where $n_{BE}(\hbar\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose-Einstein factor for an effective phonon frequency $\hbar\omega$ that describes the vibrational degrees of freedom for $\hbar\omega \gg kT$. From the fit, we obtain $n_0 = 2.377(3)$, $A = 0.019(7)$, and $\hbar\omega = 711$ cm^{-1}, a reasonable value for the average phonon frequency in diamond (see below for a discussion of the error bars).

The thin solid line in Fig. 2 linearly extrapolates the high-temperature limit of the fit (thick solid line) to the data [i.e., $n(T) = n_0 + (A/\hbar\omega)k_B T$] towards 0 K, thus indicating the refractive index in the absence of the electron-phonon interaction and thermal expansion contributions. By comparison of the thin solid line with the experimental data, we notice that albeit the measurements beyond 600 K vary almost linearly with T, the high-temperature limit of Eq. (3.1) has not yet been reached, even at 925 K. From the fit to the data, we

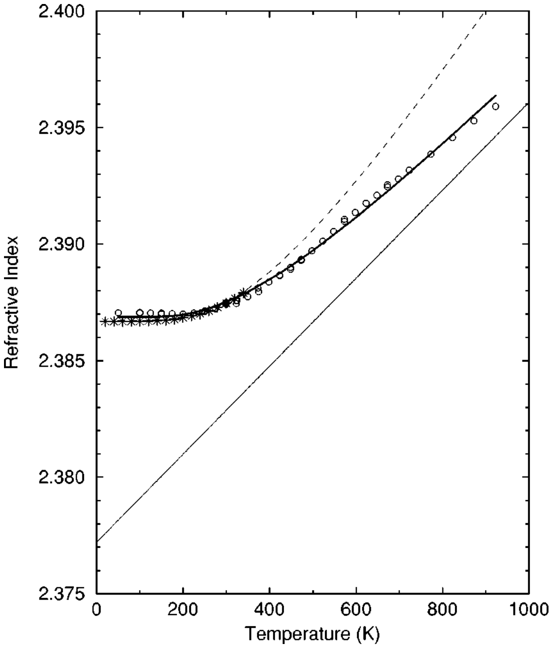

FIG. 2. Temperature dependence of the refractive index in diamond. The open circles represent the experimental data after correction for thermal expansion. The thick solid line is a fit of Eq. (3.1) to these data. The thin solid line extrapolates the high-temperature limit of the fit to the data. To illustrate the importance of the thermal expansion correction, the dashed line is a fit of Eq. (3.1) to the uncorrected data. Data from Ref. 14 are shown as asterisks.

determine a thermo-optic coefficient of $(1/n)(\partial n/\partial T)=7.1\times10^{-6}\ \mathrm{K}^{-1}$ at 925 K, more than twice as large as the value of $3.2\times10^{-6}\ \mathrm{K}^{-1}$ at 300 K.

The dashed line in Fig. 2 represents a Bose-Einstein fit to the refractive-index data (not shown) as obtained from Airy-function fits [see Eq. (2.1)] to the interference spectra with the *constant* room-temperature value for d. However, the sample thickness varies due to thermal expansion. The data shown in Fig. 2 (open circles) are therefore corrected values obtained by using the empirical analytical expression for the thermal expansion of diamond given in the recent comprehensive review of Ref. 21. The comparison between the dashed curve and the data (open circles) shows that thermal expansion effects cannot be neglected beyond 400 K.

We have performed fits to the data with Eq. (3.1) using several fixed values of $\hbar\omega$. Noticeable deviations from the experimental $n(T)$ curve occur for frequencies differing from the optimum value of 711 cm^{-1} by more than 150 cm^{-1}. This was used to determine error bars for the renormalization of the refractive index at 0 K, which was found to be $\Delta n=0.010\pm0.003$ (corresponding to $\Delta\epsilon=2n\Delta n=0.048\pm0.014$). Error bars for the thermo-optic coefficients and the fit parameters n_0 and A (see above) were determined by the same procedure. From the expected proportionality of the 0 K refractive index (dielectric function) renormalization Δn ($\Delta\epsilon$) to $1/\sqrt{M}$, we estimate an isotope shift of $\Delta n_{\mathrm{iso}}=0.0004$ ($\Delta\epsilon_{\mathrm{iso}}=0.0019$) between ^{12}C (natural) and ^{13}C diamond.

A compilation of our results and those from other studies is given in Table I. Our value for the thermo-optic coefficient at 300 K is in reasonable agreement with the earlier measurements of Refs. 12 and 14 and the theoretical prediction of Ref. 19. However, the value obtained in Ref. 15 is two times larger. The reason for this deviation is that the data in Ref. 15 were derived from a fit to high-temperature refractive-index measurements (295–784 K), which is almost linear. This fit does not properly consider the curvature of $n(T)$ around 300 K, and, consequently, is more appropriate in the high-temperature regime where, in fact, the thermo-optic coefficient agrees quite well with our result. The values for $(1/n)(\partial n/\partial T)$ of Ref. 17 are much larger than those reported in all other studies, both at 300 K ($13.3\times10^{-6}\ \mathrm{K}^{-1}$) and at high temperatures ($31.5\times10^{-6}\ \mathrm{K}^{-1}$ at 1600 K). We attribute this discrepancy to the intrinsic inaccuracy of refractive-index determinations via Brillouin scattering, as manifested by the considerable variations for $n(T)$ found in different scattering geometries (see Fig. 3 of Ref. 17), and to the fact that these data were obtained at visible wavelengths rather than in the far-infrared region. We also found that a quadratic fit, as done in Ref. 17, to our data in Fig. 2 is not adequate and leads to a significant overestimate for the thermo-optic coefficient at high temperatures.

The calculated thermo-optic coefficient of Ref. 18 is about three times larger than the observations. This is acceptable in view of the 40% error bars of this theory and the approximations that had to be made in order to handle the problem almost analytically. Although the theory of Ref. 19 agrees rather well with the measured thermo-optic coefficient at 300 K, its predictions for the refractive-index renormalization and the isotope effect at 0 K are about three times larger than our results. The origin of this deviation is presently unclear. However, it highlights the importance of experimen-

TABLE I. Thermo-optic coefficients, refractive-index renormalization, and predicted isotope effects (^{12}C vs ^{13}C) of diamond in the long-wavelength regime ([e] = experiment, [t] = theory).

$\frac{1}{n}\frac{\partial n}{\partial T}(\mathrm{K}^{-1})$ (300 K)	$\frac{1}{n}\frac{\partial n}{\partial T}(\mathrm{K}^{-1})$ (High-temperature limit)	Δn (0 K)	Δn_{iso} (0 K)	Reference
$3.2(7)\times10^{-6}$ [e]	$7.1(7)\times10^{-6}$(925 K) [e]	0.010(3)[e]	0.0004	This work
5×10^{-6} [e]				12
4.04×10^{-6} [e]				14
6.7×10^{-6} [e]	6.7×10^{-6} (784 K) [e]			15
11×10^{-6} [t]				18
5.12×10^{-6} [t]		0.0291 [t]	0.0011 [t]	19

tal tests even for *ab initio* calculations which are generally assumed to be very accurate. We hope that our results will stimulate further theoretical and experimental work on this issue.

IV. CONCLUSIONS

We have measured the refractive index of diamond up to 925 K. From a Bose-Einstein fit to these data, we have determined the thermo-optic coefficient at different temperatures, the refractive-index renormalization at low temperatures, and an estimate of the isotope effect on n. The results clarify the discrepancies between various earlier experiments and calculations.

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